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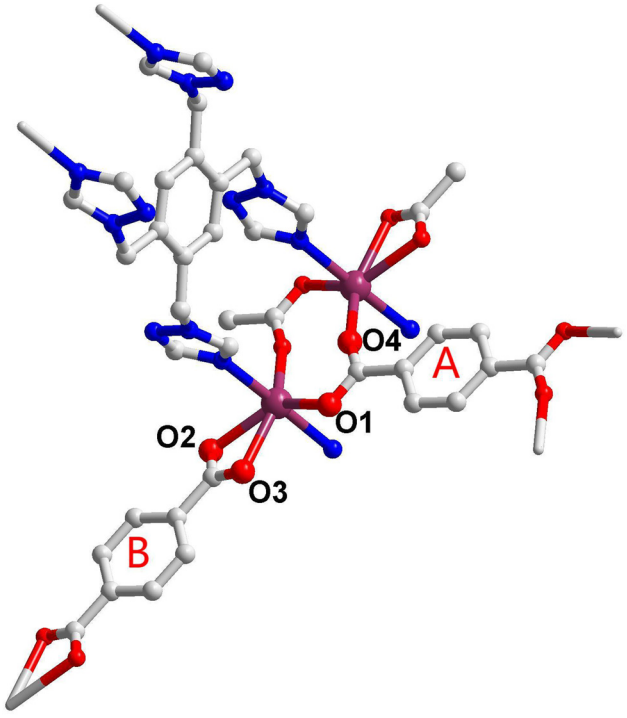
The crystal structure of poly[(μ$_2$-terephthalato-κ^4*O*,*O*′: *O*″,*O*‴)-(μ$_4$-terephthalato-κ^4*O*:*O*′:*O*″:*O*‴)-{μ$_4$-(1,2,4,5-tetrakis(1,2,4-triazol-1-ylmethyl)-benzene-κ^4*O*:*O*′:*O*″,*O*‴)}dicadmium(II)] – water – acetronitrile (1/2/2), $C_{38}H_{36}N_{14}O_{10}Cd_2$



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Abstract

$C_{38}H_{36}N_{14}O_{10}Cd_2$, triclinic, $P\bar{1}$ (no. 2), a = 10.220(2) Å, b = 10.685(2) Å, c = 10.777(2) Å, α = 84.18(3)°, β = 72.02(3)°, γ = 75.28(3)°, V = 1082.3(4) Å^3, Z = 1, $R_{gt}(F)$ = 0.0268, $wR_{ref}(F^2)$ = 0.0732, T = 293(2) K.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.29 × 0.25 × 0.24 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	1.06 mm^{-1}
Diffractometer, scan mode:	Rigaku Saturn 724, ω
θ_{max}, completeness:	27.9°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13,220, 5081, 0.021
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 4850
$N(param)_{refined}$:	317
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4]

A part of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Terephthalic acid (0.017 g, 0.1 mmol), 1,2,4,5-tetrakis(1,2,4-triazol-1-ylmethyl)-benzene (0.04 g, 0.1 mmol) and cadmium(II) acetate (0.023 g, 0.1 mmol) were added to the mixture of water (3 mL) and acetonitrile (7 mL) in a Teflon-lined stainless steel reactor. The mixture was heated at 413 K for three days, and then slowly cooled down to room temperature. Colorless crystals of the title compound were obtained.

Experimental details

Absorption corrections were applied by using multi-scan program [1]. Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program using Intrinsic Phasing and refined with the ShelXL [4] refinement package. The H atoms bonded to C atoms were fixed, with C–H distance of 0.93 Å; and/or positioned geometrically in the riding-model approximation, with C–H distance of 0.97 Å; U_{iso}(H) = 1.2U_{eq}(C), U_{iso}(H) = 1.5U_{eq}(O).

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Cd1	0.10338 (2)	0.36516 (2)	0.85953 (2)	0.02185 (6)
O1	−0.12044 (19)	0.3947 (2)	0.8383 (2)	0.0413 (5)
O2	0.3438 (2)	0.2290 (2)	0.7716 (2)	0.0455 (5)
O3	0.1755 (2)	0.2144 (2)	0.6919 (2)	0.0405 (5)
O4	0.1455 (2)	0.4721 (3)	1.0112 (2)	0.0525 (6)
N1	0.1588 (3)	−0.4840 (2)	1.6969 (2)	0.0364 (5)
N2	0.2742 (4)	−0.3785 (4)	1.5259 (4)	0.0703 (10)
N3	0.1365 (3)	−0.3577 (2)	1.5306 (2)	0.0369 (5)
C2	−0.1965 (2)	0.4702 (3)	0.9282 (2)	0.0288 (5)
C3	−0.3544 (2)	0.4877 (2)	0.9646 (2)	0.0264 (5)
C6	0.2823 (4)	−0.4554 (4)	1.6260 (4)	0.0636 (11)
H6	0.3664	−0.4881	1.6472	0.076*
C8	0.3009 (3)	0.1835 (2)	0.6921 (3)	0.0315 (5)
C9	0.4052 (3)	0.0878 (2)	0.5928 (2)	0.0309 (5)
C10	0.0006 (3)	0.0935 (2)	1.4043 (2)	0.0315 (5)
H10	0.0012	0.1572	1.3388	0.038*
C11	0.0426 (3)	−0.0357 (2)	1.3695 (2)	0.0266 (5)
C13	−0.4432 (3)	0.5673 (3)	1.0662 (3)	0.0381 (6)
H13	−0.4057	0.6121	1.1111	0.046*
C14	0.0863 (3)	−0.0715 (2)	1.2265 (2)	0.0355 (6)
H14A[a]	0.1879	−0.1056	1.1967	0.043*
H14B[a]	0.0414	−0.1390	1.2187	0.043*
H14C[b]	0.1723	−0.1399	1.2083	0.043*
H14D[b]	0.0128	−0.1047	1.2113	0.043*
C15	0.0711 (3)	−0.4213 (3)	1.6313 (3)	0.0358 (6)
H15	−0.0242	−0.4222	1.6534	0.043*
C16	0.3558 (3)	0.0119 (3)	0.5287 (3)	0.0411 (7)
H16	0.2590	0.0196	0.5477	0.049*
C17	0.0425 (3)	−0.1309 (2)	1.4664 (2)	0.0293 (5)
C22	0.0792 (4)	−0.2732 (3)	1.4348 (3)	0.0472 (8)
H22A	−0.0052	−0.2966	1.4312	0.057*
H22B	0.1482	−0.2869	1.3493	0.057*
C24	0.5497 (3)	0.0758 (3)	0.5637 (3)	0.0414 (7)
H24	0.5836	0.1265	0.6060	0.050*
C25	−0.4119 (3)	0.4203 (3)	0.9000 (3)	0.0385 (6)
H25	−0.3524	0.3660	0.8328	0.046*
N5[a]	0.0472 (3)	0.0383 (2)	1.1441 (2)	0.0299 (6)
N6[a]	−0.0911 (3)	0.0843 (3)	1.1479 (3)	0.0420 (6)
N7[a]	0.0426 (3)	0.2091 (2)	1.0167 (2)	0.0325 (6)
C7[a]	−0.0883 (3)	0.1861 (3)	1.0703 (3)	0.0366 (7)
H7[a]	−0.1690	0.2385	1.0531	0.044*
C18[a]	0.1242 (3)	0.1139 (3)	1.0658 (3)	0.0324 (6)
H18[a]	0.2215	0.1016	1.0481	0.039*
N4A[b]	0.1196 (18)	0.2073 (15)	1.0188 (17)	0.0325 (6)
N5A[b]	0.1094 (18)	0.0340 (16)	1.1408 (19)	0.0299 (6)
N6A[b]	0.2382 (17)	0.0563 (16)	1.1208 (19)	0.0420 (6)
C7A[b]	0.2374 (19)	0.1705 (17)	1.057 (2)	0.0366 (7)
H7A[b]	0.3068	0.2168	1.0418	0.044*
C18A[b]	0.0372 (18)	0.1271 (18)	1.0782 (19)	0.0324 (6)
H18A[b]	−0.0549	0.1346	1.0765	0.039*
O6	0.5457 (6)	0.0841 (5)	0.8968 (5)	0.159 (2)
H6A	0.6322	0.0571	0.8540	0.239*
H6B	0.5029	0.1357	0.8488	0.239*
N4[c]	0.7325 (17)	−0.249 (2)	0.7327 (19)	0.151 (4)
C1[c]	0.6128 (19)	−0.235 (2)	0.749 (2)	0.116 (4)
C19[c]	0.481 (3)	−0.255 (4)	0.735 (4)	0.127 (6)
H19A[c]	0.4810	−0.2394	0.6460	0.190*
H19B[c]	0.4018	−0.1953	0.7897	0.190*
H19C[c]	0.4738	−0.3418	0.7614	0.190*
N8[d]	0.7420 (11)	−0.3494 (13)	0.6303 (12)	0.151 (4)
C4[d]	0.4824 (16)	−0.219 (2)	0.7783 (19)	0.127 (6)
H4A[d]	0.4098	−0.2354	0.7477	0.190*
H4B[d]	0.4788	−0.1275	0.7699	0.190*
H4C[d]	0.4676	−0.2457	0.8682	0.190*
C5[d]	0.6274 (12)	−0.2934 (13)	0.6968 (13)	0.116 (4)

[a]Occupancy: 0.879 (3), [b]Occupancy: 0.121 (3), [c]Occupancy: 0.384 (8), [d]Occupancy: 0.616 (8).

Comment

The 1,2,4-triazole containing ligands are considered as interesting heterocycles because of their strong coordination ability to transition metal ion and effective biological importance [5–8]. Complexes containing 1,2,4-triazole ligands often possess rather peculiar structures and specific properties [9–13]. For example, as the flexible tetra(triazole) ligand, 1,2,4,5-tetrakis(1,2,4-triazol-1-ylmethyl)-benzene (ttyb) has many advantages: (i) strong coordination ability; (ii) more potential coordination points and coordination modes; (iii) can rotate around the central C–C bond and adopt different conformations [14–16]. On the basis of the above considerations, we choosed the ttyb ligand as a functional ligand and employed "mix-ligand" synthetic strategy to explore the assembly with "mixed" d the ttyb and aromatic polycarboxylate ligands. In this context, we reacted ttyb with Cd^{2+} ions, then employed terephthalic acid (PTA) ligand as an auxiliary ligand, which features one three-dimensional pillared layered structure, namely $[Cd_2(PTA)_2(ttyb)](H_2O)_2(CH_3CN)_2$.

The most obvious structural feature of the title complex is the pillared layered structure where the layers are formed of cadmium atoms bridged by the dicarboxylate while the pillar is the ttyb ligand. The secondary building unit (SBU) node consists of a cadmium dimer in distorted octahedral geometry formed by two bidentate bridging carboxylates from two PTA^{2-} anions, two chelating PTA^{2-} anions, and two pairs of ttyb ligand in *trans*-positions pointing along the c-axis. The linear dicarboxylate extends the two-blade paddle-wheel $Cd_2(COO)_4$ unit to produce a perfect 2D square grid. The Cd···Cd distance is 4.322 Å. It is worth mentioning that PTA^{2-} ligands in the title structure adopt two different coordination modes: one PTA^{2-} ligand (defined as A type) adopts a $(\eta^1{:}\eta^1) - (\eta^1{:}\eta^1) - \mu_4$ coordination mode that the PTA^{2-} ligand acts as a four connector connecting

four cadmium atoms, whereas the other (defined as B type) adopts a $(\eta^1{:}\eta^1)$ – $(\eta^1{:}\eta^1)$ – μ_2 coordination mode. Due to the different coordination modes of the carboxylate within the dimeric subunits, the (4, 4) grid deviates from being a square with sides of 8.0 and 12.5 Å. Ligand ttyb acts as μ_4-bridge linking four Cd(II) ions, and connect the 2D layer to extend to a 3D structure. The Cd–O lengths are in the range of 2.286(2)–2.465(2) Å. The Cd–N lengths are in the range of 2.295(2)–2.311(2) Å. The second key feature of the structure is the interpenetration because long ttyb ligands were incorporated. Two ttyb pillars at each cadmium node connect the layers to generate one of the two identical 3D-frameworks. The motifs are mutually interdigitated to create a stable 3D assembled framework. Comparing the title structure (I) with {[Cd(PTA)$(ttyb)_{0.5}(H_2O)$]} (II) [15], both of which prepared from the same starting reactants, some important similarities and differences can be found as follows: (i) The structure. The title structure is three-dimensional pillared layered structure, while II is two-dimensional structure. (ii) The composition. There are free molecules of acetonitrile molecules in I, but absence in II. This is because of the use of the mixed H_2O-acetonitrile solvent for synthesis of I, while mixed H_2O-1,4-dioxane solvent for that of II. (iii) The coordination mode of ttyb ligand. In I, ligand ttyb function as a tetradentate ligand to coordinate with four Cd atoms. In II, ligand ttyb function as a bidentate ligand to bind with two Cd atoms, another two 1,2,4-triazol groups do not take part in the coordination. (iv) The coordination geometry of Cd(II) ion. It is in octahedron for I, while in tetragonal pyramid for II.

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Conflict of interest statement: The author declares no conflicts of interest regarding this article.

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